PB85-161552

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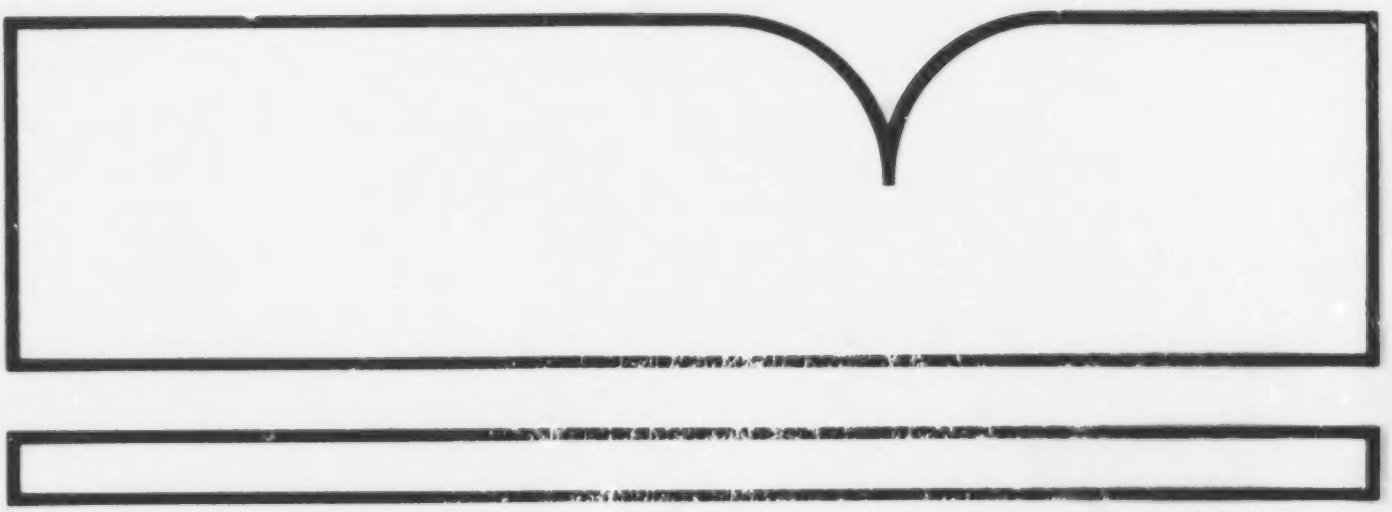
Feb 85



U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-161552

EPA/600/D-85/030
February 1985

A COMPARISON OF PROCEDURES TO DETERMINE ADSORPTION CAPACITY OF VOLATILE ORGANIC COMPOUNDS ON ACTIVATED CARBON

Richard J. Miltner
Drinking Water Research Division
Municipal Environmental Research Laboratory

and

O. Thomas Love, Jr.
Water Supply Branch, Region VI
Dallas, Texas 77570

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
Cincinnati, Ohio 45268

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TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA/600/D-85/030	2.	3. RECIPIENT'S ACCESSION NO. PB85 161552/AS
4. TITLE AND SUBTITLE A Comparison of Procedures to Determine Adsorption Capacity of Volatile Organic Compounds on Activated Carbon		5. REPORT DATE February 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Richard J. Miltner and O. Thomas Love, Jr.		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Drinking Water Research Division Water Engineering Research Laboratory U.S. Environmental Protection Agency Cincinnati, Ohio 45268		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same as 9.		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/14
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

Numerous volatile organic compounds (VOCs) are under regulatory consideration for inclusion in the National Primary Drinking Water Standards. Adsorption is a cost-effective treatment technology for control of VOCs. Adsorption capacities were determined for fifteen VOCs in distilled and field waters using different procedures. A macroisotherm procedure, testing 100 gallons of water, was compared with a bottle isotherm procedure, testing 250 mL of water. While procedures were comparable, conventional bottle procedures were better suited to water utility laboratories. Scale was found to have no significant effect on adsorption capacity.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 15
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

A COMPARISON OF PROCEDURES TO DETERMINE ADSORPTION CAPACITY OF VOLATILE ORGANIC COMPOUNDS ON ACTIVATED CARBON

Richard J. Miltner
Environmental Engineer
Drinking Water Research Division
Water Engineering Research Laboratory
Cincinnati, Ohio 45268

O. Thomas Love, Jr.
Sanitary Engineer
Water Supply Branch, Region VI
Dallas, Texas 77570

United States Environmental Protection Agency

A number of volatile organic compounds (VOCs) are regulated or are under consideration for regulation in drinking water. Maximum contaminant levels for trihalomethanes were promulgated in 1979.[1] Recommended maximum contaminant levels for nine VOCs were proposed in 1984,[2] and numerous compounds, volatile in nature, were cited in an Advanced Notice of Proposed Rulemaking in 1983.[3] In addition to aeration, adsorption onto granular activated carbon (GAC) is a cost-effective treatment process for many of these compounds.[4] As a result, laboratories will seek to develop GAC adsorption capacity data as one step in the process of comparing adsorption to other processes, in order to make comparisons among carbons, or as the first step in the design of the adsorption process.

A review of the literature found little discussion on standard procedures for adsorption capacity tests, but much discussion and presentation of adsorption capacity data. A significant contribution in this area was made by Randtke and Snoeyink, wherein design and interpretation of GAC adsorption capacity tests were examined.[5]

This paper presents GAC adsorption capacity data, expressed as equilibrium isotherms, for a number of VOCs under regulatory consideration. Several procedures were employed; each is described and resulting data and procedural ease are compared.

MATERIALS

Adsorbent Filtrasorb 400* was employed. It was stored in manufacturer's 50 pound bags or in glassware under Teflon seal. After sieving, samples were stored in glassware under Teflon seal.

Adsorbates All VOCs were reagent-grade quality. VOCs were stored in their manufacturer's containers, or aliquots were taken and stored in Teflon-sealed glassware.

Solution Waters Distilled water and two field waters were studied. Field waters were filtered though a bed of sand or mixed-media bed of sand and anthracite coal. One, Ohio River water, provided a moderate total organic carbon (TOC) background. The other, a gravel pit water, provided a relatively high TOC background. A capillary column, gas-

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*Mention of commercial products does not constitute approval or endorsement by U.S. EPA.

chromatographic profile found the latter to be heavily laden with low- to mid-molecular weight organic compounds relative to typical surface water profiles.[6] These waters are described in Table 1. All waters were stored in glass under Teflon seal.

Reaction Vessels All contact surfaces were glass, Teflon, or stainless steel. Glassware was distilled water washed and fired to 400°C; stainless steel and Teflon were distilled water rinsed several times and air dried. Other materials used in pumps or meters were not observed to produce interfering chromatographic peaks or to exhibit VOC demand.

ANALYTICAL METHODS

A purge-and-trap gas chromatographic procedure was used to determine VOC concentrations.[7] TOC concentrations were determined by using a Dohrmann/Envirotech DC-54 low-level analyzer.

EXPERIMENTAL PROCEDURES

VOC Preparation Microliter volumes of VOC were injected into water during mixing. Mixing was briefly stopped, water was added to eliminate a headspace, the vessel was Teflon sealed, and mixing continued until steady-state, mg/L concentration stock solutions were achieved. Volume dilutions were mixed in a similar manner until ug/L concentration working solutions were achieved. Selected VOCs were studied to determine the required mixing time for stock solutions of mg/L concentrations; VOC stock solutions were typically mixed two days.

Care was taken to dose below solubility limits and to avoid the use of intermediate co-solvents to aid in solution. A co-solvent was used, however, in the case of lighter-than-water VOCs. An ethanol/ water, V/V ratio of approximately 1/8000 was used in preparing mg/L stock solutions. Ethanol has been reported to be non-adsorbable[8], thus it was not believed to compete with VOCs for adsorption sites.

GAC Preparation The adsorbent was grab sampled from 50-pound bags, placed in a ball mill, pulverized for 30 days and graded using US-standard sieves and a sieve shaker. 50x200 mesh adsorbent was stored in Teflon-sealed glassware. Distilled water was added to a weighed amount of 200x400 mesh adsorbent until desired volumes were reached. The slurries were mixed for three days and stored in glass-stoppered bottles. Non-graded, grab-sampled adsorbent was termed 12x40 mesh as per manufacturer's specifications.

Adsorption Capacity Isotherm Procedures Two procedures were employed. One was a bottle (250 mL) isotherm, batch procedure using three mesh sizes: 200x400, 50x200 or 12x40. The other was a large volume (100 gallon), recirculating procedure, termed macroisotherm, using only 12x40 mesh GAC. The macroisotherm procedure attempted to evaluate whether capacities developed from large-volume isotherms better correlated with field capacities than those from bottle-size isotherms.

Bottle Isotherms Required volumes of slurry containing 200x400 mesh adsorbent were added to 250 mL centrifuge tubes via dispensing pipets, providing a range of adsorbent doses. As required, make-up water was added to each dosed tube or undosed control tube to keep VOC dilution constant. Ug/L working solutions of VOC were pumped into each

tube. The tubes were Teflon-sealed without headspace. Mixing was provided by a device that tumbled the tubes end-over-end at room temperature at a rate of 10-12 rpm. At the termination of tumbling, tubes were centrifuged at 2000 rpm for 60 minutes at constant temperature (20-21°). Following centrifugation, samples were withdrawn by pipet and transferred to Teflon-sealed vials. For selected VOCs, control tubes were withdrawn during tumbling, centrifuged and sampled to verify no loss of VOC over the reaction period. For selected VOCs, identically GAC-dosed tubes were withdrawn during tumbling, centrifuged and sampled to establish the required time to equilibrium. Equilibrium was defined as the time beyond which changes in subsequent concentrations were within expected analytical precision for the procedures employed, generally ±6%. [7]

Control of volatilization during adsorbent separation was necessary. Paper filtration, with or without a vacuum, was not attempted, assuming excessive losses. Filter-disk separation was abandoned after significant volatile loss of trichloroethylene (TCE) as observed. No attempt was made to determine whether the loss was attributable to an uptake of TCE by the filter material or whether volatilization of TCE was enhanced by passing the filters. Centrifugation was found to produce no loss of VOC that could be distinguished from expected analytic precision.

Required weights of 50x200 mesh adsorbent were added to 250 mL screw-cap bottles, providing a range of adsorbent doses. Ug/L working solutions of VOC were pumped into each dosed or control bottle. The bottles were Teflon-sealed headspace-free and tumbled as described. Following tumbling, the bottles stood for 16 to 20 hours to allow for gravity settling of the adsorbent. Following settling, samples were collected by pipet, as described. Both VOC stability over the reaction period and time to equilibrium were determined, as described. Bottle isotherms utilizing 12x40 mesh adsorbent were handled in an identical manner, with the exception of gravity settling time, which was rapid.

Macroisotherms In this procedure, VOC-spiked water was pumped from a 100-gallon stainless steel tank, passed through a meter, up through a column containing 12x40 mesh adsorbent, and returned to the tank (see Figure 1). The vessel was filled with water in an upflow manner, with the headspace being displaced along the walls of the conical top through the funnel. During recirculation, a mg/L concentration VOC stock solution was introduced at the apex while an identical volume of water was withdrawn at a sample tap to maintain a headspace-free condition. Recirculation continued until a ug/L concentration working solution was uniformly diluted throughout the vessel. Control tests with selected VOCs showed uniform dilution to occur in two hours or less. 12x40 mesh adsorbent was weighed, added to the column, flushed for several minutes to fill void spaces, affixed to the vessel, and recirculating water was directed from the bypass line to the column. The vessel was sampled below the column until the VOC concentration was shown to have reached equilibrium. As a sample was collected, unspiked make-up water was introduced from the funnel to maintain a headspace-free condition; the resulting dilution (approximately 1/13000) was insignificant. Equilibrium was defined as described. For chlorobenzene, samples were collected above and below the column to confirm exhaustion of the adsorbent. Several vessels were operated in this manner providing a range of carbon doses. Vessels operated without adsorbent were sampled over time to verify no loss of VOC during the time required to reach equilibrium.

RESULTS AND DISCUSSION

Time-to-Equilibrium Determination The time required to reach equilibrium was determined for several VOCs. Generally, for each VOC studied in bottle tests, the time required for the smallest adsorbent weight to equilibrate was determined, as it requires a longer time than larger adsorbent weights.[5] In some cases, a minimum time to equilibrium was not determined; rather, tests revealed that equilibrium had occurred before the first, time-sequenced sample was collected. Table 2 presents mean values of time-to-equilibrium conditions for bottle isotherm tests. In support of the literature, the required time was dependent on particle size.[5] While a mean three hours or less were required to reach equilibrium using 200x400 mesh adsorbent, a mean reaction time of near three days was utilized to ensure equilibrium conditions. Similarly, longer-than-required times were utilized for larger-mesh-sized adsorbent to ensure that equilibrium had been reached. A typical time-to-equilibrium test is seen in Figure 2 where eleven days were required to reach equilibrium under the cited conditions.

Generally, each macroisotherm vessel was sampled to determine time to equilibrium for each VOC studied. Using this procedure, the time required for the smallest adsorbent weight used for each VOC was not necessarily the longest, as recirculation rate varied inversely with headloss through the column which, in turn, varied with adsorbent weight. Figure 3 shows a typical time-to-equilibrium test requiring approximately 800 gallons throughput under the cited conditions.

Comparison of Procedures Data were fitted to the Freundlich equilibrum expression:

$$q_e = KC_e^{1/n}$$

where q_e = adsorbent equilibrium in mg VOC adsorbed/gram adsorbent; C_e = adsorbate equilibrium in mg VOC/L solution water; and K and 1/n are experimentally determined constants. Data were fited to the Freundlich expression using the method of least squares. For comparative purposes, a prediction band was calculated for the line. The prediction interval estimates the range of a new q_e, for a given C_e, on the basis of the fitted line. The family of q_e intervals over the experimental range of C_e provides a prediction band.[8,9] A 95 percent confidence level was chosen. Procedures were compared by testing whether the Freundlich line fitted to data from one procedure, i.e., the family of new q_e's, fell within the prediction band fitted to data from another procedure. One such comparison is seen in Figure 4 where the data from the bottle isotherm procedure utilizing 200x400 adsorbent fell within the prediction band about data from the macroisotherm procedure. Conversely, the latter fell within the prediction band of the former. Other representative comparisons are seen in Figures 5 and 6. Generally, data from macroiostherm and bottle isotherm procedures were comparable using 95 percent prediction bands, as were data from bottle isotherm procedures utilizing different mesh-size adsorbent. When procedures were not comparable using 95% confidence levels, they were if 90 percent confidence levels were used.

Because procedures were considered comparable, the macroisotherm procedure was abandoned in preference to the bottle procedures, as the latter are less labor-, time-, space- and sample-intensive. These studies

showed scale to be of little importance in developing adsorption capacity data. Laboratories seeking to develop such data can do so with generally available laboratory equipment and supplies.

Results Table 3 summarizes relevant adsorption capacity data from isotherm studies of VOCs in distilled water using Filtrasorb 400. In addition to the Freundlich constants, the least squares correlation coefficient and range of experimental data are given. In the application of these, or any Freundlich data, the user must note that extrapolation beyond the experimental range of Ce leads to wider intervals about q_e than would be the case if confined within the range. By definition, the interval about K is relatively wide as $K = q_e$ at $C_e = 1.0$ mg/L, i.e., beyond the experimental range of C_e in these studies. Where several procedures were used, the least squares fit given in Table 3 was made using the summation of data points, as listed.

Similar data are cited in Table 4 for VOCs in solution waters of variable TOC concentration. An examination of Freundlich K constants for tetrachloroethylene (PCE) and TCE suggests that adsorption capacity decreases with increasing TOC, i.e., with increasing competition for adsorption sites. Figure 7 supports this, wherein the 95 percent prediction bands about TCE in distilled water (TOC <0.1 mg/L) and in filtered Ohio River water (TOC = 1.97 mg/L) demonstrate no coincidence over the range of experimental data. Both VOCs in filtered gravel pit water (TOC = 8.39 mg/L) show similar separation of prediction bands over the experimental range. For 1,1,1-trichloroethane (TCA) and cis-1,2-dichloroethylene (CIS), however, no significant differences in capacity appear to exist over the experimental range. An example of this may be seen in Figure 8 for cis-1,2-dichloroethylene in high- and low-TOC waters. Why compounds of higher adsorption capacity (PCE or TCE) are more affected by competative matrices than compounds of lower capacity (TCA or CIS) is not well understood and needs further investigation.

ACKNOWLEDGEMENTS

The authors appreciate the efforts of Kenneth Kropp, James Horton, Christian Nyberg, Michelle Hamlin, Ihor Melnyk and John Lauch for conducting isotherm studies, Bradford Smith for performing organic analyses, Herbert Braxton and Kim Fox for their assistance with graphics, Leown Moore, James Westrick and Alan Stevens for technical review of the paper, and Pat Pierson and Maura Lilly for typing the paper. At the time of these studies, O. Thomas Love was with the Drinking Water Research Division.

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TABLE 1

Properties of solution waters used in isotherm studies

Water	Mean pH	Mean TOC mg/L	Turbidity ntu
Distilled	6.68	0.09	< 0.1
Filtered Ohio River	7.98	1.97	< 1.0
Filtered Gravel Pit	8.04	8.39	< 1.0

TABLE 2

Bottle isotherm reaction times, days

Mesh Size	Mean Required Time	Mean Test Time
200 x 400	0.125	2.8
50 x 200	4.5	7.1
12 x 40	15.7	23.9

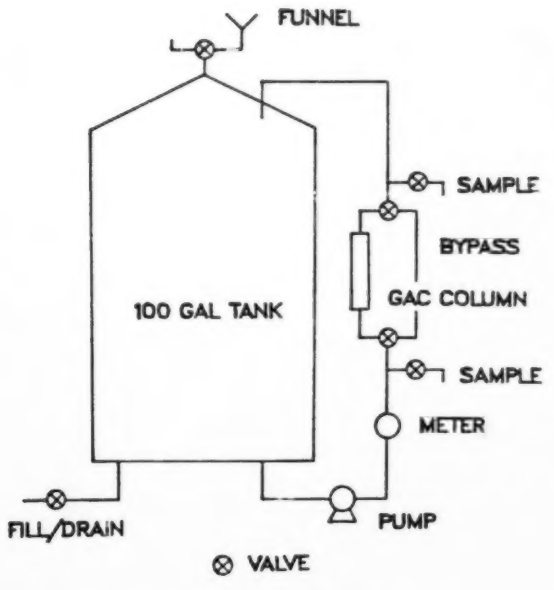

Figure 1. Macroisotherm apparatus.

TABLE 3

Freundlich isotherm values
distilled water, Filtrasorb 400

Compound	K mg/g	1/n	r	C_e Range ug/L	Number Points	Procedures
tetrachloroethylene	143	0.52	0.983	3.6-421	29	M,BS
trichloroethylene	56.0	0.48	0.991	7.7-442	17	M,BL
1,1-dichloroethylene	16.5	0.52	0.998	6.9-392	6	M
cis-1,2-dichloroethylene	11.7	0.59	0.981	5.1-615	38	M,BS,BL
trans,1-2-dichloroethylene	17.0	0.51	0.983	14-415	10	BL
1,1,1-trichloroethane	13.2	0.53	0.976	15-860	10	M
1,2-dichloroethane	5.1	0.53	0.984	42-727	9	M
1,1-dichloroethane	7.9	0.64	0.996	26-495	11	BL
carbon tetrachloride	23.6	0.59	0.968	9.1-429	18	M
benzene	50.0	0.53	0.998	3.2-462	10	BL
ethyl benzene	120	0.44	0.958	5.6-158	12	BA,BS
chlorobenzene	101	0.34	0.991	15-353	6	M
o-dichlorobenzene	407	0.50	0.986	14-208	8	M
p-dichlorobenzene	472	0.65	0.891	5.7-284	21	BA,BS
1,2-dibromomethane (EDB)	25.3	0.51	0.924	13-123	12	BA,BS

M = macroisotherm; B = bottle isotherm
S = 200x400 mesh; A = 50x200 mesh; L = 12x40 mesh

TABLE 4

Freundlich isotherm values
variable TOC, Filtrasorb 400

Compound	TOC mg/L	K mg/g	1/n	r	C_e range ug/L	Number Points	Procedures
tetrachloroethylene	<0.1	143	0.52	0.983	3.6-421	29	M,BS
	8.39	59.2	0.39	0.993	4.6-330	10	BL
trichloroethylene	<0.1	56.0	0.48	0.991	7.7-442	17	M,BL
	1.97	31.6	0.44	0.979	13-380	16	BL,BS
	8.39	24.4	0.44	0.979	13-399	19	BL,BS
1,1,1-trichloroethane	<0.1	13.2	0.53	0.976	15-860	10	M
	1.97	12.4	0.52	0.986	7.6-601	22	M,BA
cis-1,2-dichloroethylene	<0.1	11.7	0.59	0.981	5.1-615	38	M,BS,BL
	1.97	12.7	0.64	0.989	19-230	8	BL
	8.39	9.1	0.52	0.993	25-527	9	BL

M = macroisotherm; B = bottle isotherm
S = 200x400 mesh; A = 50 x 200 mesh; L = 12x40 mesh

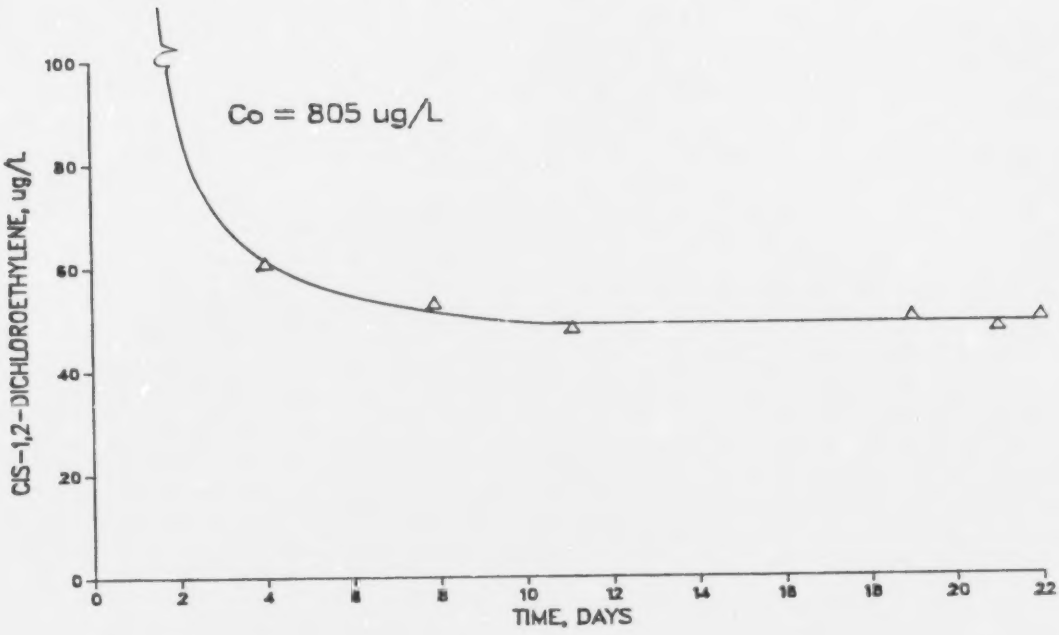

Figure 2. Time-to-equilibrium study using 12x40 mesh adsorbent and bottle isotherm procedure for cis-1,2-dichloroethylene in distilled water.

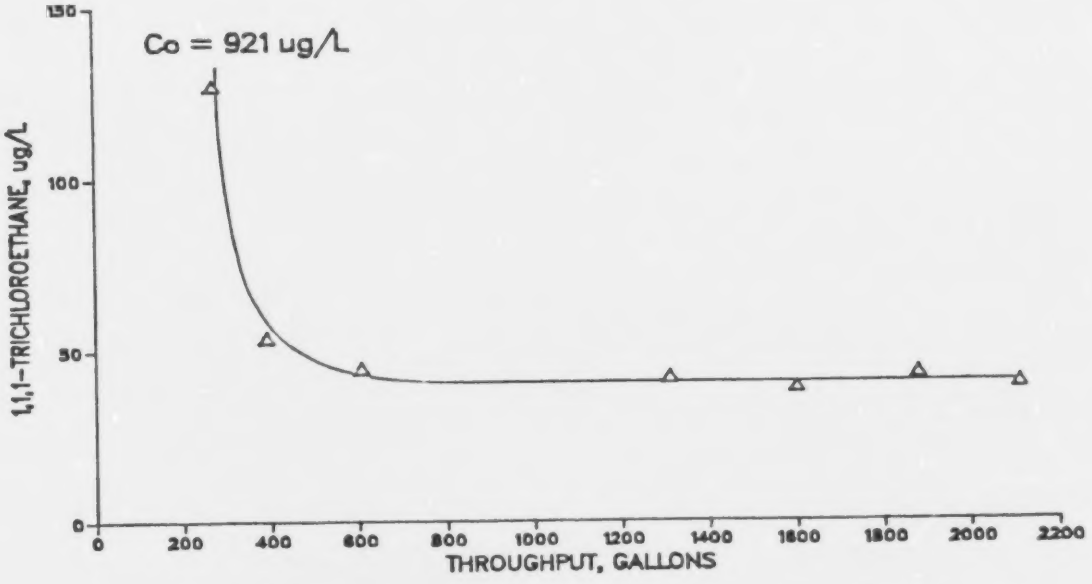

Figure 3. Time-to-equilibrium study using 12x40 mesh adsorbent and macroisotherm procedure for 1,1,1-trichloroethane in distilled water.

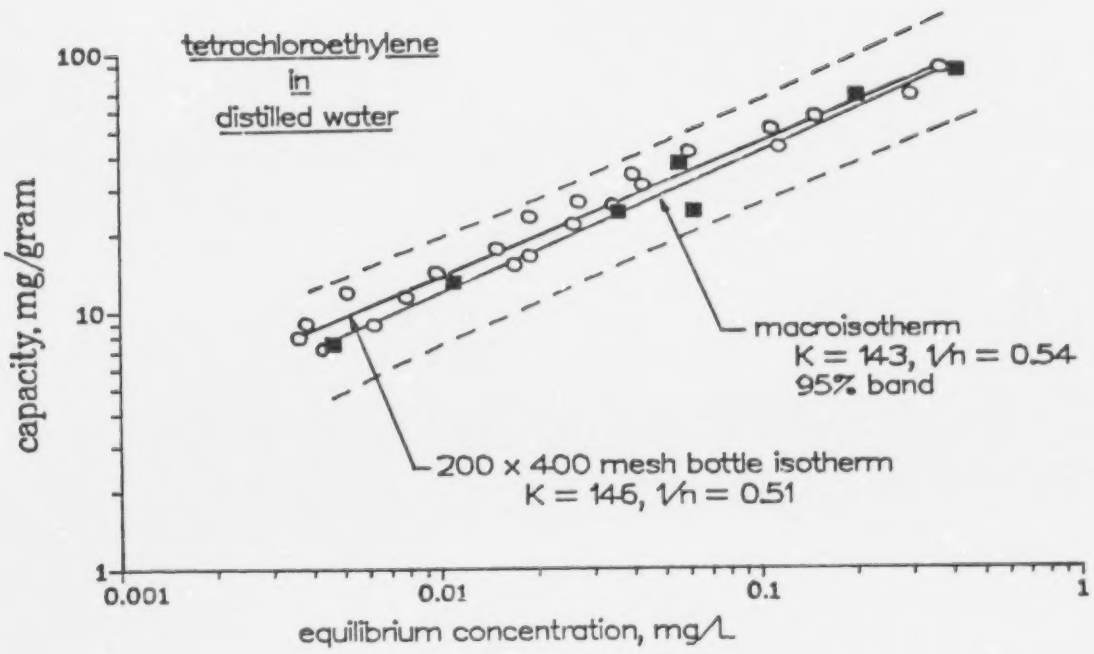

Figure 4. Freundlich isotherms for tetrachloroethylene in distilled water using different procedures.

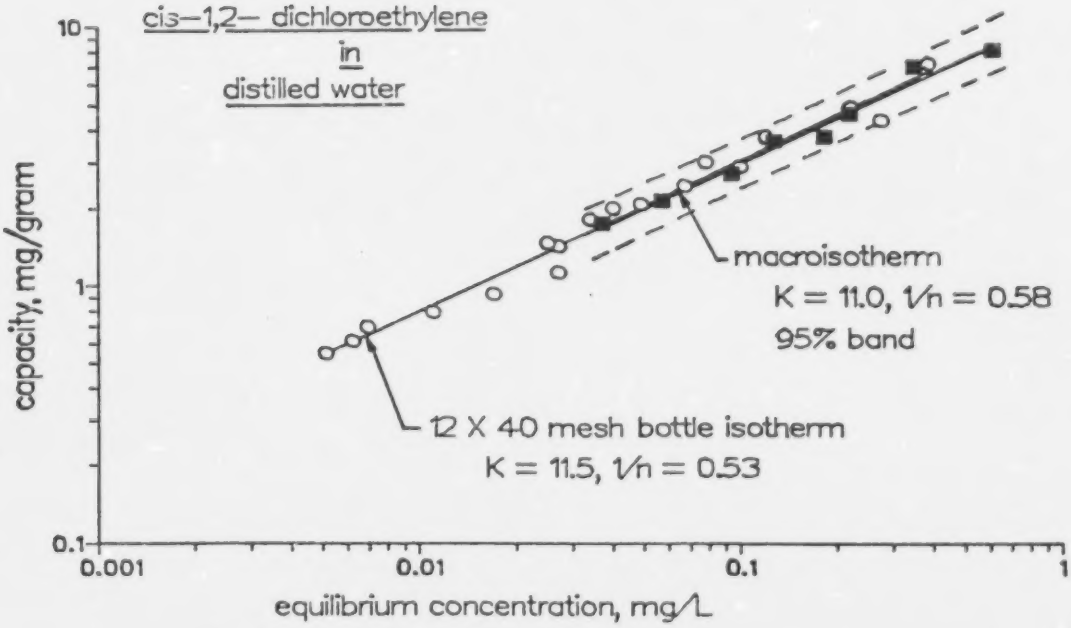

Figure 5. Freundlich isotherms for cis-1,2-dichloroethylene in distilled water using different procedures.

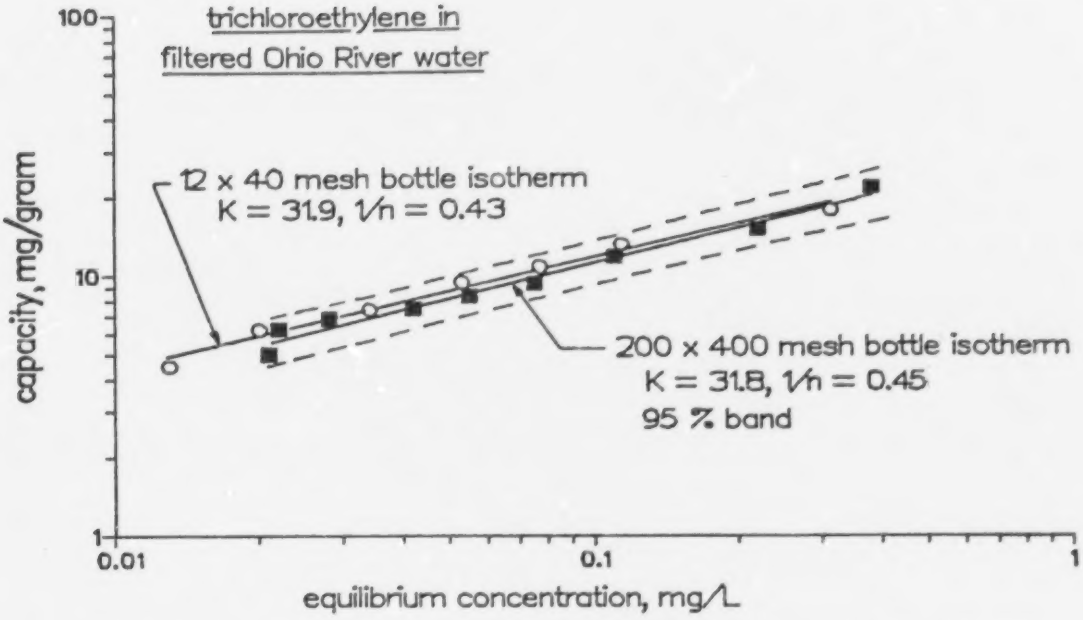

Figure 6. Freundlich isotherms for trichloroethylene in Ohio River water using different mesh-size adsorbent.

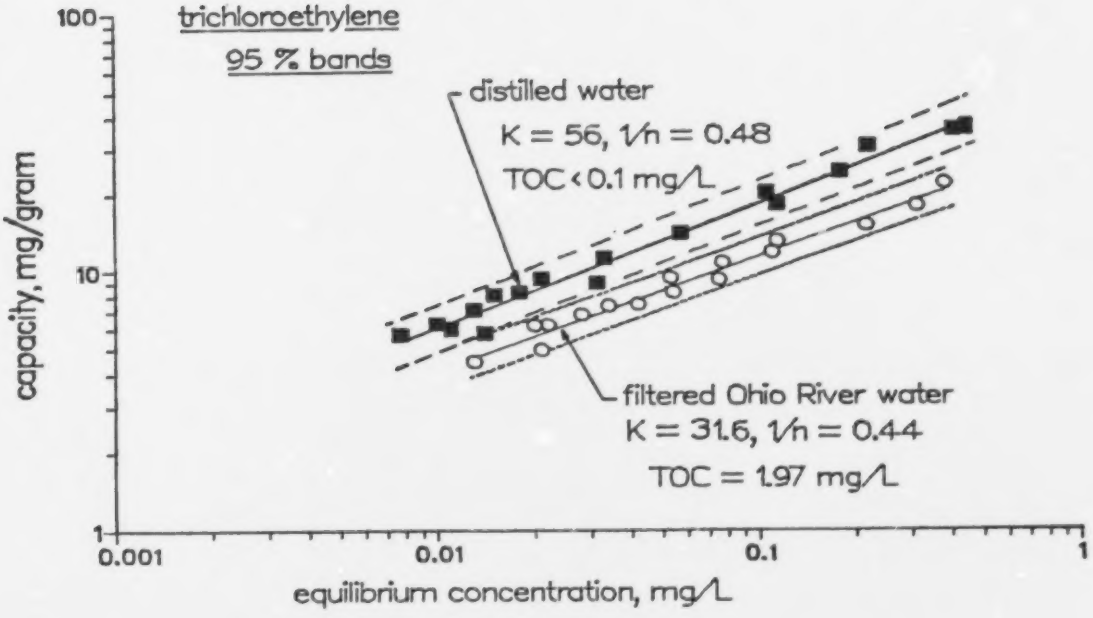

Figure 7. Freundlich isotherms for trichloroethylene.

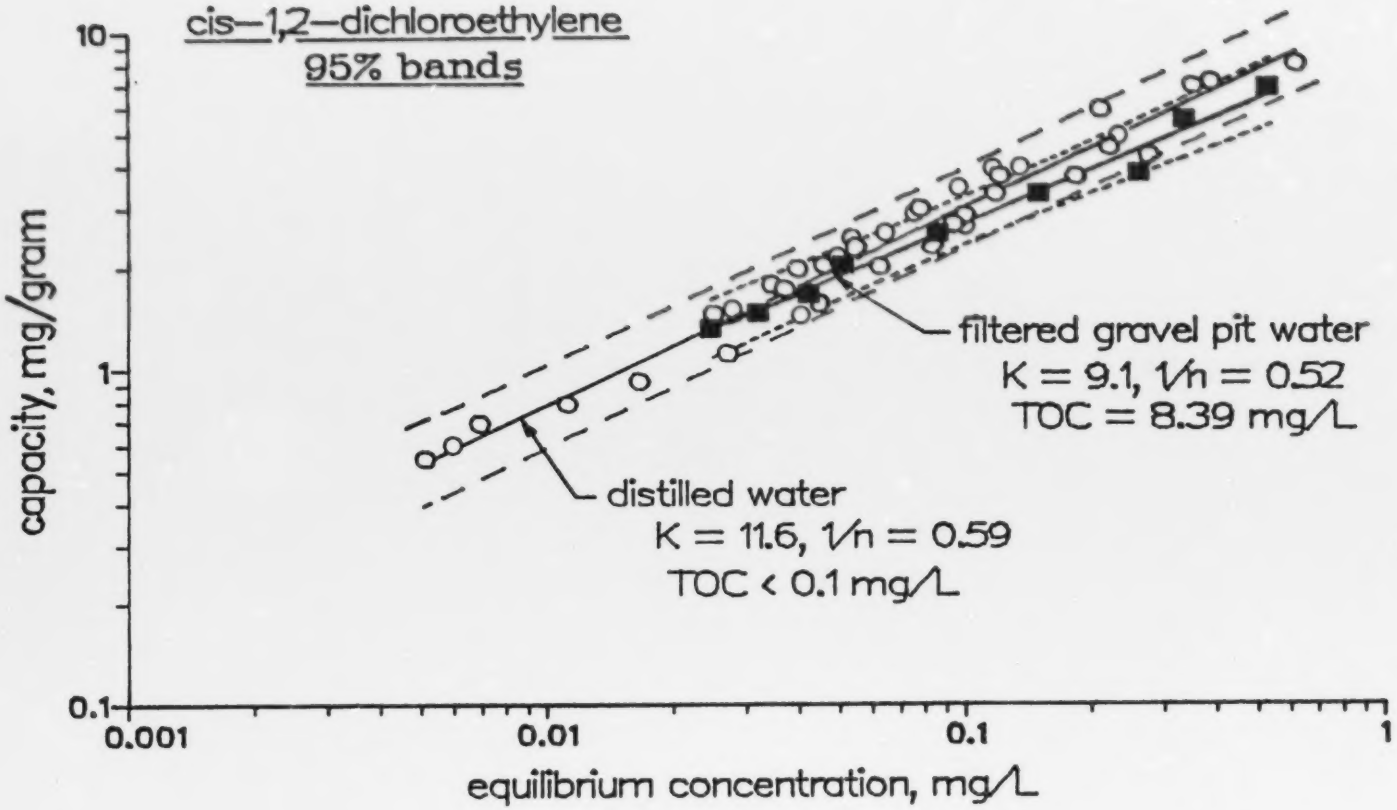

Figure 8. Freundlich isotherms for cis-1,2-dichloroethylene.